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TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental
Technology

EFFECT OF COLOURANTS ON THE PHYSICAL AND
CHEMICAL BEHAVIOUR OF POLYPROPYLENE

VÄRVAINETE MÕJU POLÜPROPÜLEENI FÜÜSIKALISELE JA
KEEMILISELE KÄITUMISELE

MASTER THESIS

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Tallinn, 2019

AUTHOR'S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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THESIS TASK

Student: Labani Dutta, 177312KVEM

Study programme: KVEM12/15- Technology of Wood, Plastic and Textiles

main speciality: Technology of plastics

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Thesis topic:

Effect of colourants on the physical and chemical behaviour of polypropylene

Värvainete mõju polüpropüleenil füüsikalisele ja keemilisele käitumisele

Thesis main objectives:

1. Preparation of samples using injection moulding.
2. Ageing at 150°C at 100 h, 200 h, 300 h and 400 h.
3. Testing- mechanical tests, colourimetry, calorimetry. Collecting and analysing the results.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Sample preparation, ageing and mechanical testing	22.12.17
2.	Colourimetry of the samples	13.05.18
3.	Calorimetry of the samples	16.12.18

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PREFACE

The basis of the project work was initiated by the company Norma AS in collaboration with Tallinn University of Technology. The experiments were carried out in Tallinn University of Technology under supervision of Prof Andres Krumme.

Several persons have contributed academically, practically and supported during the master thesis. I would therefore firstly like to thank my supervisor Prof Andres Krumme for his input, valuable time and constant support throughout the master period.

I am also grateful and thankful to Dr. Iliia Krasnou for support in conducting the experiments.

I would also like to thank Dr. Viktoria Vassiljeva for the constructive comments to the thesis.

Lastly, I would like to thank my family and friend Eujeny for always supporting me through thick and thin.

The master thesis has been an incredible way to learn about research work. This work requires a lot of support and motivation throughout the master period.

The aim of the work was to incorporate colorant (10 % by weight) in polypropylene using injection moulding and age the samples at 150°C for 100 h, 200 h, 300 h and 400 h. Mechanical tests, colourimetry and calorimetry was conducted to evaluate the change in properties of PP. Tensile stress and strain results increased compared to the pure PP. Colourimetry results obtained showed uniformity in the colour and the effect of ageing was low. The oxidation induction time decreased With the increase in accelerated ageing. The melting point increased by 30°C.

Keywords: Polypropylene, colourants, mechanical tests, colourimetry, calorimetry, oxidation induction time

List of terms

Gauge length – Initial distance between the gauge marks on the central part of the test specimen

Monomer- It is a molecule that "can undergo polymerisation, thereby contributing constitutional units to the essential structure of a macromolecule. The combination of a greater number of monomers to form a polymer is known as polymerisation.

Methyl groups- is an alkyl derived from methane, containing one carbon atom bonded to three hydrogen atoms — CH₃. Methyl groups can be of 3 forms- anion, cation and radical.

Strain at break – strain at the last recorded data point before the stress is reduced to less than or equal to 10% of the strength if the break occurs before yielding (expressed in %)

Stress at maximum load -pressure at the yield strain (expressed in MPa)

Thermoplastic- It is a plastic polymer material that becomes pliable or mouldable at a specific elevated temperature and solidifies upon cooling

Tacticity- The regularity of the macromolecular structure influences the degree to which it has rigid, crystalline long-range order or flexible, amorphous long-term disorder.

Yield Stress – Normal force per unit area of the original cross-section within the gauge length

Yield Strain – increase in length per unit original of the gauge (shown in %)

INTRODUCTION

The thesis explains effects of colorants on the injection moulded polypropylene. The work is initiated by the company Norma AS, who manufactures plastic (polypropylene or PP) covered car buckles. One of the reasons for the project work is the public demand for the coloured fasteners. The company provided six different colours to be tested.

Among the plastics there is a general family called polyolefins. Polypropylene is a polyolefin and is a versatile thermoplastic which is currently leading in the plastic industry. It is adaptable with different processing techniques which is its remarkable feature. Therefore, it can be used in many several commercial applications, including the one mentioned above.

The injection moulded specimens prepared in Tallinn University of technology and the buckles provided by the Norma AS were aged at 150°C for 0, 100, 200, 300 and 400 h. The accelerated ageing is conducted to increase the reproducibility for certifying the quality of the product. It helps to confirm the required properties of the product and correlate with outdoor conditions to achieve better lifetime of the product. (Shimizu K, Tokuta K, Oishi A, Kuriyama T, 2016)

The aged samples were tested and compared with polypropylene without colourant and ageing. Instron 5866 was used for the tensile tests via bluehill software for one of the mechanical tests. The other mechanical tests conducted was the charpy impact using 4 J hammer. The colourimetry is performed with a spectrophotometer L*a*b* colour space. For accurate thermal properties, mainly oxidation induction time was measured by differential scanning calorimetry.

The results from the tests gives an overview of the properties of colourants in polypropylene. The colourants may enhance or deteriorate mechanical characteristics of polypropylene. It is also points out the difference in the characteristics of darker and lighter range of colours. The results help to make decisions regarding durability of different coloured materials in processing and applications.

1 Polypropylene

1.1 Background

In 1954 G Natta was the first to polymerise propylene monomer to form polypropylene (PP). The macromolecules of PP contain 10,000 to 20,000 monomer units. The monomer is asymmetrical (Figure 1.1). (Tripathi, 2002)

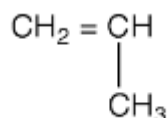


Figure 1.1 Polypropylene monomer (Tripathi, 2002)

When propylene monomer polymerises, the steric arrangement of the methyl groups linked to the other carbon atom in the chain may differ (Figure 1.2). The chain arrangement forms three basic chain structures, which are as follows:

Isotactic -the methyl groups are present in the chain are aligned in the same side of the chain. It is mostly used commercially. Since it has a regular arrangement, PP has a high degree of crystallinity, thereby forming a rigid structure.

Syndiotactic – the methyl groups are in alternating positions regarding the main chain. Syndiotactic PP is also being produced commercially using metallocene catalysts.

Atactic- the methyl groups are randomly placed regarding the main chain. This form does not crystallise due to the randomness in the structure. It is a rubbery material. (Donald, 2001)

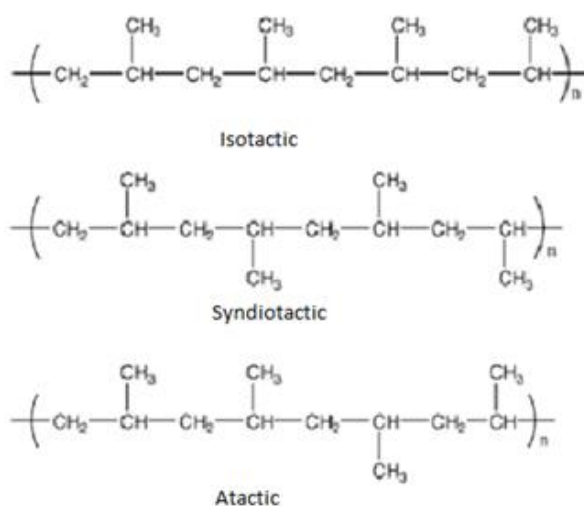


Figure 1.2 Tacticity of polypropylene (Tripathi, 2002)

1.2 Properties

The properties of commercial polypropylene generally differ as per the level of crystalline isotactic polymer and the degree of polymerisation. Polypropylenes with a 99% isotactic index are at currently used in production. The mechanical and thermal properties are dependent on the tacticity, molecular weight and its distribution, crystallinity. The mechanical properties depend on time, temperature and stress. Polymers are responsive to changes in temperatures. The features such as mechanical, thermal, chemical etc. are not considered without the knowledge of the temperature. (Matar, Hatch S, 2001)

1.2.1 Thermal Properties

1.2.1.1 Glass transition temperature and melting point

Glass transition temperature affects the mechanical properties of PP at a specific temperature. Macromolecules are immobile at low temperature and when heated the restricted macromolecular zones becomes movable. The material becomes soft form solid state at glass transition temperature because some molecular segments become more mobile. Glass transition temperature is measured using a dynamic mechanical, thermal analyser (DMTA) or differential scanning calorimeter (DSC). Glass transition temperature of polypropylene is 258-270K. (Tripathi, 2002)

Isotactic polypropylene molecules tend to form super-molecular structures when cooled to temperatures below the melting point (crystallisation temperature). At the crystallisation temperature, the macromolecules organise themselves into crystals, and systematic crystalline region and disorganised amorphous regions are formed. The development of the crystals may occur immediately or may be induced due to foreign particles such as a nucleating agent. (Wiley V.C.H, 2016)

The thermal conductivity of polypropylene is quite low compared to the metals. High temperatures can degrade the polymer before the material melts in an extruder for processing. Therefore, thermal properties should be selected for a relevant process of manufacturing. The thermal properties are listed in Table 1. (Othman, 2008)

Table 1: Thermal properties of Polypropylene (Othman, 2008)

Thermal properties of Polypropylene	Values
Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	0,1382
Processing temperatures($^{\circ}\text{C}$)	200-250
Onset decomposition temperatures($^{\circ}\text{C}$)	280
Thermal diffusion constants($\text{m}^2\text{sec}^{-1}$)	$0,9 \times 10^{-7}$
Specific heat	0,46
Mould temperature ($^{\circ}\text{C}$)	30-80
Thermal diffusivity ($\text{m}^2\text{C}^{-1}\text{sec}^{-1}$)	$6,5 \times 10^{-9}$
Typical moulding temperature:	
Cylinder ($^{\circ}\text{C}$)	250
Mould ($^{\circ}\text{C}$)	60
Heat distortion ($^{\circ}\text{C}$)	120
Factor	338
Moulding set up time (seconds)= factor x max thickness (m)	

1.2.1.2 Oxidation

The oxidation of PP is highly susceptible due to the tertiary hydrogen group on the carbon. If PP is not stabilised, then it oxidises faster than PE, which reduces molecular weight. The beginning stage in the active investigation of the oxidation of polypropylene is the estimation of the degree of oxidation of the polymer as a function of time. (Halley, 2009)

Polymer oxidation occurs through a free radical chain reaction. The homolytic cleavage of the carbon-hydrogen or then again carbon-carbon covalent bond in the polypropylene chain is the result from mechanical stress, heat, or the presence of oxygen or metal catalyst residues; every atom gets one electron from the two-electron covalent bond, delivering two free radicals, each with an unpaired electron. The chain reaction is propagated through the development of a hydroperoxide, joined by the development of another free radical. The slow step determines the oxidation rate (Figure 1.3). The free radical formed from the deliberation of tertiary hydrogen is more stable than those formed from the abstraction of primary hydrogen, because of the possibility of carbon atoms along the chain to give electrons to the electron-insufficient radical. (Maier C; Calafut, 1998) (Calhoun, 2007)

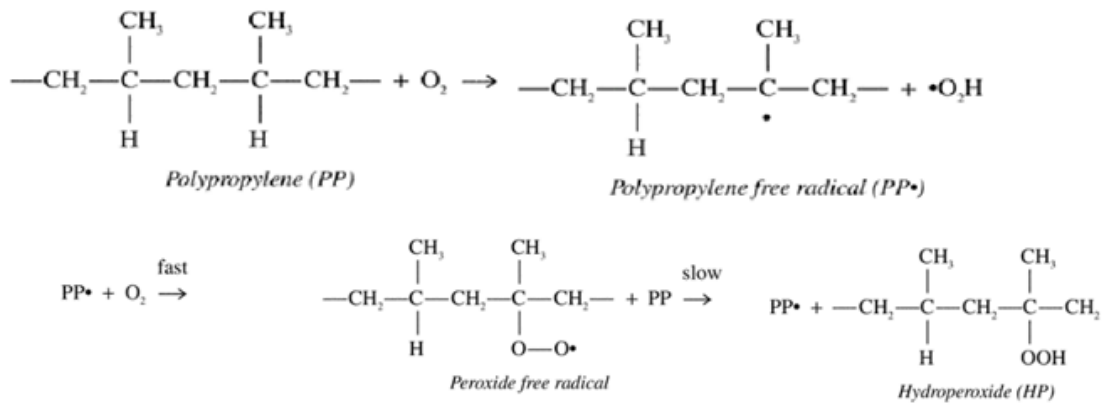


Figure 1.3 Oxidation scheme (Maier C; Calafut, 1998)

1.2.1.3 Ageing

The adjustments in the polymer properties under the distinctive environmental and preparing conditions are named ageing. Polymers have been known to illustrate two sorts of ageing: chemical and physical. Artificial ageing is thermal degradation, photooxidation, etc. and the progressions are associated with deterioration and lead to molecular chain scission as well as cross-linking. The outcome is cracking and chemical integration of polymers. Examination of accelerated artificial ageing, therefore, for convenience referred to as ageing, is critical because of this aide for better understanding and expectation of long-term behaviour of polymers in useful applications. (Borovanska *et al.*, 2014)

The chemical responses associated with thermal degradation lead to physical and optical property changes in respect to the at indicated properties. Thermal degradation includes changes to the atomic weight (and molecular weight distribution) of the polymer, and common property changes include:

- Reduced malleability and embrittlement
- Chalking
- Colour changes
- Cracking
- A general decrease in most other attractive physical properties (Zeus Industrial Products inc., 2005)

Measurements and investigations show that ageing of PP leads to structural changes. It shows complex behaviour in the rearrangements of the crystalline process leading to an increase in the tensile properties. The crystalline morphology determines the semi-crystalline nature of polypropylene. (Rogers C.E, 1972) The influential factors are average molar mass, molar mass

distribution and chain regularity as well as the processing parameters and dynamics of crystallisation. (Struik L.C.E, 1978) Ageing is observed through the changes in density, the crystallinity of PP which can be determined by DSC. The changes in the temperature regions due to the ageing of polypropylene is shown in Table 2. (Tomlins P, 1996)

Table 2: Mobility regions for physical ageing of polypropylene (temperature indications refer to homopolymers based on standard catalyst systems)(Fiebig J, Gahleitner M, 1999)

Region	Temperature (°C)	Changes
Glassy	0-4	Density, mechanics(slightly)
Amorphous mobility	50-100	Density, mechanics, the order in amorphous-regions (significantly)
Recrystallisation	162-167	Melting point, crystallinity

The ageing of PP can be accelerated due to the presence of soluble manganese ions in an additive. (Müller, 2003) Ageing also develops pronounced superstructure, which has a noticeable effect on the mechanical and optical properties of PP. The nature of the polymer, the processing conditions and temperature level of ageing has an essential role in determining various changes in the characteristics of PP. Investigations show ageing of PP is mesomorphic,(Cavallo D, Geiusepp, Luigi Balzano, Azzurri F, Bras W, Gerrit W. Peters and Alfonso, 2010) and higher mobility results in non-spherulitic morphology also affecting the impact strength. (Gahleitner, 2002)

The coloured masterbatch does not have a significant influence on the melting point of PP except for the white masterbatch. There is hardly any significant difference in the melting temperature of coloured and compounded samples, which gives an overview of the volume percentage of crystallinity compounded and coloured PP samples. The addition of masterbatch and compounding reduces crystallinity. Therefore it different types of pigments attributes to a different level of nucleating activity resulting in various degrees of crystallisation. (Sahin and Yayla, 2005)

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1.2.2 Mechanical Properties

Mechanical properties can be considered as the reaction of a material when it is exposed to several mechanical loading conditions. Since the polymers are viscoelastic materials, they, demonstrate a moderate position between viscous fluids and elastic solids in their reaction to mechanical loads. (Izdebska, Thomas J, 2016)

1.2.2.1 Tensile properties

In the presence of nucleating agents, the tensile strength of isotactic PP increases by 70%. Spherulite size is another factor which affects the tensile strength. It decreases with the increase in the size of the spherulite during extrusion. The yield stress depends on the crystalline phase and degree of orientation. (Emmanuel R, Verdu J, 2009)

The strain at break decreases from 650 % to 10 % at 190°C, which shows the extreme degradation of PP. Therefore the injection temperature should be controlled. (Strapasson R, Amico S.C, 2005)The increase in temperature increases the elongation indicates PP did not degrade (Figure 1.4).

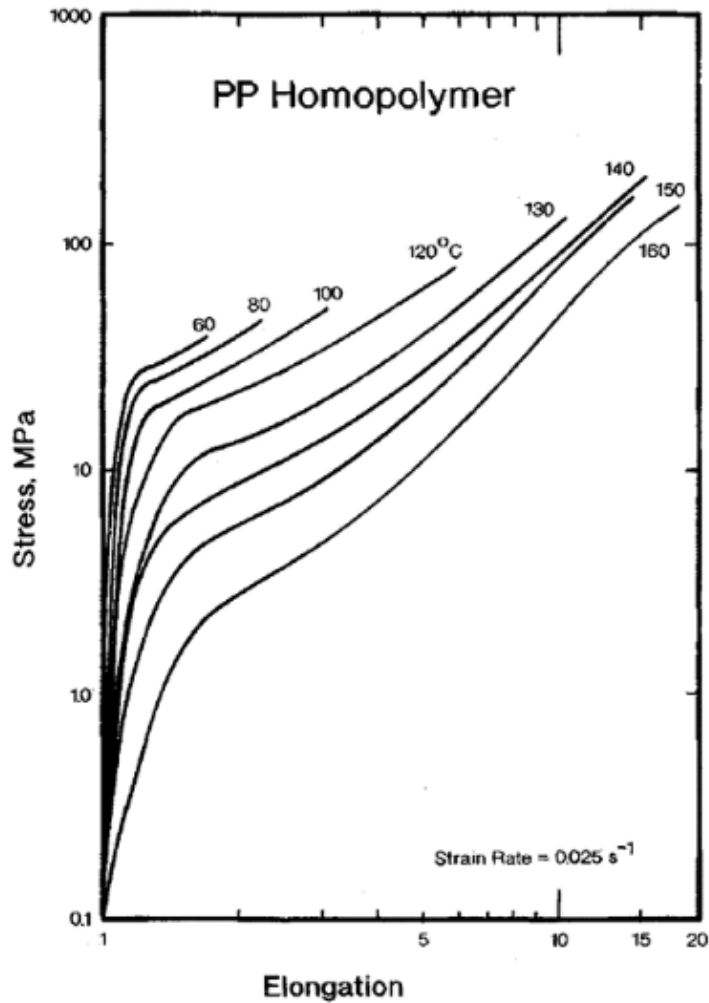


Figure 1.4 A schematic tensile stress /strain curve for PP homopolymer at various temperatures (Throne J, 1996)

There are only a few investigations conducted on the effect of the colour masterbatch type and concentration on mechanical properties of PP. Concentration of colour masterbatch effect on the yield stress of PP.

It was found that yield stress decreases when the masterbatch content is up to 0.5%. Later it was observed that the increase in masterbatch content recovers the yield stress and increases with concentration. The yield strain decreases with the addition of the masterbatch content, and it also depends on the colour compound. (Sahin and Yayla, 2005)

The results of the tensile test demonstrated a higher modulus for the polypropylene without colourants than the materials with colourant included. The blue coloured specimens show a 3.7% decrease, magenta a 4.1% decline, yellow has the most minimal with a 0.6% decrease in modulus when contrasted with the regular PP. The stress at yield was higher for the materials with the colourant included, aside from the blue, which was generally near the polypropylene. The stress at

yield for blue demonstrates a 0.3% lessening, magenta a 1.6% increase, yellow a 3.7% expansion when contrasted with the polypropylene. The test results for the per cent elongation changed slightly. The blue demonstrates a 0.2% increase, magenta a 0.6% decrease, and yellow a 1.8% expansion when contrasted with the regular polypropylene. The stress at break demonstrates an increase for all materials except blue, which has a 1.6% decrease. Magenta shows a 1% increase and yellows a 2% increment when contrasted with the standard material. The per cent elongation at break for blue demonstrates a 2.2% reduction, magenta a 15.2% decrease and yellow a 23.2% decrease when contrasted with the natural material. (Krisher J.A, 1997)

1.2.2.2 Impact strength

The second order transition temperature of PP homopolymer is -10°C . The decrease in the impact strength is at around 0°C . The isotactic polypropylene shapes large spherulites when it solidifies from a melt, when nucleating agents are not in use and which can initiate defects in the material under stress. (Wypych G, 2016) The impact strength of PP is measured using various methods, but none of them can predict performance satisfactorily. Incorporation of the rubbery phase helps to improve the impact strength of PP. Toughness increases with higher rubber content, and its transition from ductile to brittle failure occurs at lower temperatures. (Tripathi, 2002)

1.3 Additives for PP

1.3.1 Antioxidants and stabilisers

Oxidative degradation in PP leads to the decrease in molecular weight, viscosity, loss of several mechanical properties, embrittlement, discolouration. Therefore, antioxidants are used to prevent oxidation of PP. It combines with free radicals or reacts with hydroperoxides to restrict oxidation of PP.

According to the performance required during processing and application requirements, antioxidants are chosen. There are two kinds of antioxidants, which are as follows:

- Primary antioxidants- It is also called radical scavengers. Hindered phenolics, secondary aromatic amines etc. are few examples. The reactive OH (hindered phenolic) or NH (secondary aromatic amine) group donates hydrogen to carbon, oxygen, or peroxy free radical forming stable PP.

Secondary antioxidants- It is also called peroxide decomposers. It restricts PP oxidation by decomposing hydroperoxides. Phosphites and thioesters are the most common. Both the types reduce hydroperoxides to a stable alcohol species in an oxidation-reduction reaction, and the phosphite or thioester oxidises to a phosphate or sulfoxide, respectively. Researchers have found that the elastic modulus and malleable quality somewhat progress within the nearness of the antioxidant, whereas the elongation at break was significantly enhanced. (Sankar V, 2016)

Polypropylene is also light and heat sensitive. PP degrades in the presence of sunlight, which results in cracking, embrittlement, chalking, discolouration, and the loss of mechanical properties such as impact strength, tensile strength, and elongation. Therefore, there are two types of stabilisers which are as follows:

- Light stabilisers-To avoid or hinder the photodegradation of polymers, UV screeners and safeguards were utilised to either physical screen UV radiation, or assimilate UV energy and then release that energy as heat. UV absorbers can be inorganic or organic. Benzophenones and hindered amines are mostly used in PP. It is essential for the PP to be compatible with the light stabiliser as it is used in high concentrations. (Zuo and Finnegan, 2016)
- Heat stabilisers-Hindered Amine Stabilizers (HAS) and phenolic antioxidants (AOs) are used as stabilisers to restrict the thermo-oxidative PP. (Gijsman, 2002)

1.3.2 Colourants

Colour gives an aesthetic appeal to all plastic products; therefore, they are in almost every plastic application. There are different qualities of colour, such as warm, soft, bright or pleasant. Colours always influence the perception of customers. Colourants used in plastics are usually dyes and pigments. (Chirayil T, 2016)

Dyes are organic compounds which are soluble in plastic. They are not compatible with polyolefin and often bleed out. They have application in oriented or cross-linked polypropylene.

Pigments are insoluble and can be organic or inorganic. They are available in various forms such as dry powder, colour concentrates, liquids and pre-coloured resins). (Gastinel J, Kenny F.C, 2017)

Table 3 gives the list of various pigments and their uses.

Table 3: Overview and examples of organic and inorganic colourants (Tolinski, 2015)

Colour	Type	Chemical Base	Common Pigment Designations	Application Notes
White	Inorganic	Titanium oxide	White 6	Standard pigment, in rutile form and UV absorption
Black	Inorganic	Carbon black	Black 7	Channel blacks purer and costlier than furnace blacks, plus greater weatherability
Red	Inorganic	Iron oxides	Red 101	Inexpensive, dull reds and browns
Red	Organic	Azo/ diazo	Red 177 and 220	Food use approval (US FDA), expensive but effective
Orange	Inorganic	Cadmium sulfoselenide	Orange 20	Heavy-metal content; expensive but extremely heat-stable
Yellow	Inorganic	Cadmium sulfide	Yellow 35 and 37	Heavy-metal content; expensive but extremely heat stable
Yellow	Organic	Azo/ diazo	Yellow 93 and 95	Weatherable
Green	Inorganic	Chrome (III) oxide	Green 17	Weak greens; excellent weatherability at low cost
Green	Organic	Phthalocyanine green	Green 7 and 36	Inexpensive, stable, bright, and transparent
Blue	Inorganic	Cobalt aluminate	Blue 28	Excellent weatherability and higher cost, comparison to ultramarine blue
Blue	Organic	Phthalocyanine blue	Blue 15	Cheap, stable, bright and transparent; food approvals (US FDA)
Violet	Inorganic	Ultramarine Violet	Violet 15	Limited weatherability; weak acid/base resistance
Violet	Organic	Quinacridone	Violet 19	Fair stability; food-use approvals (US FDA)

Prerequisites of colourants

- the simplicity of incorporation and dispersion
- inertness under processing conditions (visible and invisible thermal fatigue)
- physical and chemical inertness towards the polymer
- compatibility with other additives (antagonism/ synergism)
- satisfactory performance during the intended service life of the plastic product
- non-toxicity

- capacity to be available in waste plastic things without causing broad ecological disturbance(Wolf R., 2017)

The most urgent assignments are to utilise colouring as an:

- Element of design
- Element of marking
- Element of protection (Coleman B.D, 2003)

1.3.2.1 Types of colour preparations

Either a liquid or solid colour preparation is chosen for the colouring of plastics. There are two conceivable outcomes for a solid colour preparation, either a fine or a granulated structure, the last known as a masterbatch. (Hewitt, 2007)

Granulated colour Preparations/ Masterbatch

Most of the present-day plastic items are prepared by injection moulding. By and large, the appeal of the article is essential, and it tends to be significantly affected by the colouring of the neat polymer. Since 90% of injection moulding companies utilise solid-phase masterbatches to colour their items, it is vital to examine how they impact the presence of the result. (Schaub, 2009)

Masterbatch is a solid or liquid additive for plastics with specific concentrations of pigments, dyes etc. It is used for colouring plastics and for imparting other properties to plastics, i.e. additive masterbatch. It is added to the polymer in the granular form before extrusion or injection moulding.

A masterbatch comprises of:

- Polymer as carrier
- Colourants
- Dispersing agent
- If necessary, additives, for example, stabilisers, nucleating agents, antistatic agents, lubricants, etc. (Müller, 2003)

Earlier pigments were used for colouring which refers to dry, solid colouring materials which are suspended in the form of liquid for preparation of paint, ink or several dyes. But nowadays masterbatch is preferred more than using raw pigments since it is available in pellets form which can be stored, moved or used easier than the powdered dyes. Masterbatches are designed and engineered for optimal dispersion, which facilitates colour consistency throughout the final product in a large amount, whereas pigment does not disperse well enough. In masterbatch, less amount of pigment is required than when added raw.

Notwithstanding appearance, solid-phase masterbatches can likewise influence flame resistance, UV steadiness, and in specific cases, mechanical properties. The colour shade of a product is just a single piece of its appearance. Shading equity (regardless of whether there are any colouring inhomogeneity marks) is similarly as critical. Because of solid phase masterbatches, the scattering of the colourants can be necessary; however, it is just a single piece of the entire blending process. A few elements impact the homogenization of solid-phase masterbatches, for example, the preparing parameters, the design of the injection moulding screw, the utilisation of additional dynamic and static blenders, and the properties of the material and masterbatch used to injection-mould the parts. The targeted assessment of the homogenization of different masterbatch formulas and segments is a critical and a new field of research. (Mark A, Spalding, 2018)

The raw materials are one or more additives, weighed and blended with molten wax and non-wax polymer. The non-wax polymer has a higher melting point than the melted wax, and the mixture is extruded to form granules, which can be used with a matrix polymer for properties or processes (Figure 1.5). (Mantzivis L.N, 2008)



Figure 1.5 Scheme of production of masterbatch (Mantzivis L.N, 2008)

1.4 Colourant interaction with polypropylene

Colourants may either weaken or strengthen the effects of other ingredients in the compound. It can also undermine the properties of the resin, such as a low purity grade of blue phthalocyanine may cause premature ageing of PP fibres. Pigments are used for appearance, opacification, protection and identification of polymers, and it can alter the ageing characteristics of the polymer. It can affect the electrical and mechanical properties of the resin due to poor dispersion. The polymer oxidation may catalyse due to oxidised pigments leading to adverse interactions between pigments and polymer stabiliser. Both physical and chemical properties polymer can be affected due to poor dispersion of pigment. These effects are difficult to detect with time and under degradation with their colour properties. Polyolefins containing carbon black shows a sharp decrease in the efficiency of stabilisers when their thermal stabilities are measured at high temperatures. The pigments should be evaluated at a broader range of temperature to give more accurate results. (Tolinski, 2015)

Aim and objectives

The main aim of the study is to observe the effect of thermal ageing on the properties of polypropylene regarding the type of colour.

Objectives

- ✓ Preparations of samples using injection molding
- ✓ Ageing of the samples for 100h, 200h, 300h and 400h at 150°C
- ✓ Mechanical testing- tensile tests and Charpy impact test
- ✓ Colorimetry testing
- ✓ Calorimetry testing
- ✓ Observations of the overall results of the tests

2 Experimental

The whole experimental was planned as three goals, which are as follows:

- Preparation of the samples using colourants by injection moulding
- Accelerated ageing of the specimens kept at elevated temperature
- Testing via three methods -Mechanical testing, colourimetry and calorimetry

2.1 Materials

The materials are provided by Norma AS. PP is the matrix polymer used for all colourants. There are five different colourants, which are Cambrian green, Linen, Damson, New Market Tan, Magnolia and PP Hostacom (Black, in granules for direct use for injection moulding) (Figure 2.1).

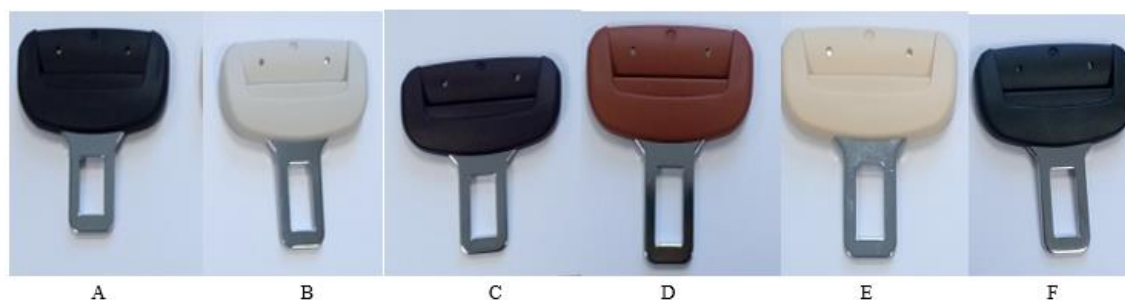


Figure 2. 1 Samples produced by the company. A. Cambrian Green B. Linen C. Damson
D. Newmarket TAN E. Magnolia F. Black (Author's photo)

Fifty samples were injection moulded for each colourant, and the pure PP was for reference. The coloured masterbatch pellets (10% by weight) and pure PP (90% by weight) were mixed mechanically in a container on a roller for 10minutes before injection moulding.

2.2 Injection moulding

The samples were prepared using Wittman Battenfeld (BA 230) injection moulding machine (Figure 2.2). Pure polypropylene and five colourant masterbatch were injections moulded using the same parameters. The temperature for the zones was 210°C -220°C and the setting time was 10 seconds. Cleaning compound was used to clean the barrel. The material was fed to the hopper and ejected out of the nozzle for few times. Then the injection moulding machine was set at automatic mode,

and the test specimens were prepared (dog-bone shaped according to ISO 527-1:2012, type 1B) (Figure 2.3).

The pure PP sample was prepared to use as a reference for the other colours.



Figure 2.2 Injection moulding machine (Author's photo)

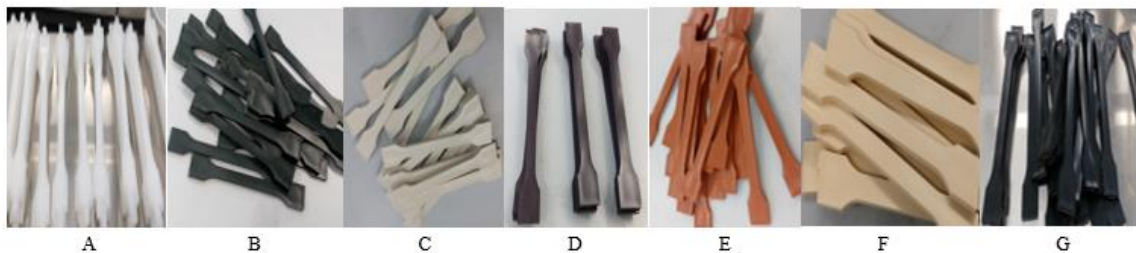


Figure 2.3 Coloured samples prepared by injection moulding A. Pure PP B. Cambrian green C. Linen D. Damson E. Newmarket Tan F. Magnolia G. Black (Author's photo)

2.3 Ageing of the specimen

The samples were aged in an automatic oven (Model: Snol). The PP test specimens were kept under 150°C for 0 h, 100 h, 200 h, 300 h and 400 h. The pure PP melted at such high temperature and had to be removed from the oven. It contaminated a few specimens. The damson coloured samples also melted to some extent at 100 h and 200 h, but surprisingly, the samples at 300 h and 400 h did not melt (Figure 2.4). The car buckles produced by the company were also aged, respectively, at 150°C for the same period for reference (Figure 2.1).



Figure 2.4 Damson coloured sample partially melted after 100 h (Author's photo)

2.4 Mechanical tests

2.4.1 Tensile testing

The tensile tests were followed using the standard ISO 527-1:2012. The test specimens are of type 1B by the standard and were prepared as described above (2.2). The sample was placed between the grips taking care to align the longitudinal axis of the testing machine (INSTRON 5866) (Figure 2.5). The clamps were tightened evenly and firmly to avoid the slippage of the test specimen and movement of grips during the test (gripping pressure can fracture or squash the test specimen). The distance between the clamps was set at 115 mm. The test speed of the machine was 50 mm/min. Blue hill software was used for the preparation of graph to calculate tensile stress, tensile strain, modulus etc. The tensile testing was performed on the specimen (5 pieces each colour) kept in an oven at 150°C for 0 h, 100 h, 200 h and 300 h.



Figure 2.5 Tensile testing machine (INSTRON 5866) (Author's photo)

2.4.2 Charpy impact strength

The Charpy impact tests were followed using the standard ISO 179:1993 (E). The test specimens are notched (Figure 2.7), and the height and width of the samples are 4mm and 8mm, respectively. The Charpy impact strength is expressed in KJ/m^2 . The samples were mounted horizontally and supported unclamped at both ends of the testing machine (Zwick Gmbh & co kg.) (Figure 2.6) The specimen is struck releasing a hammer, and if a breakage does not occur, then the heavier hammer is used until failure occurs. The calibration of the equipment and data were recorded manually.

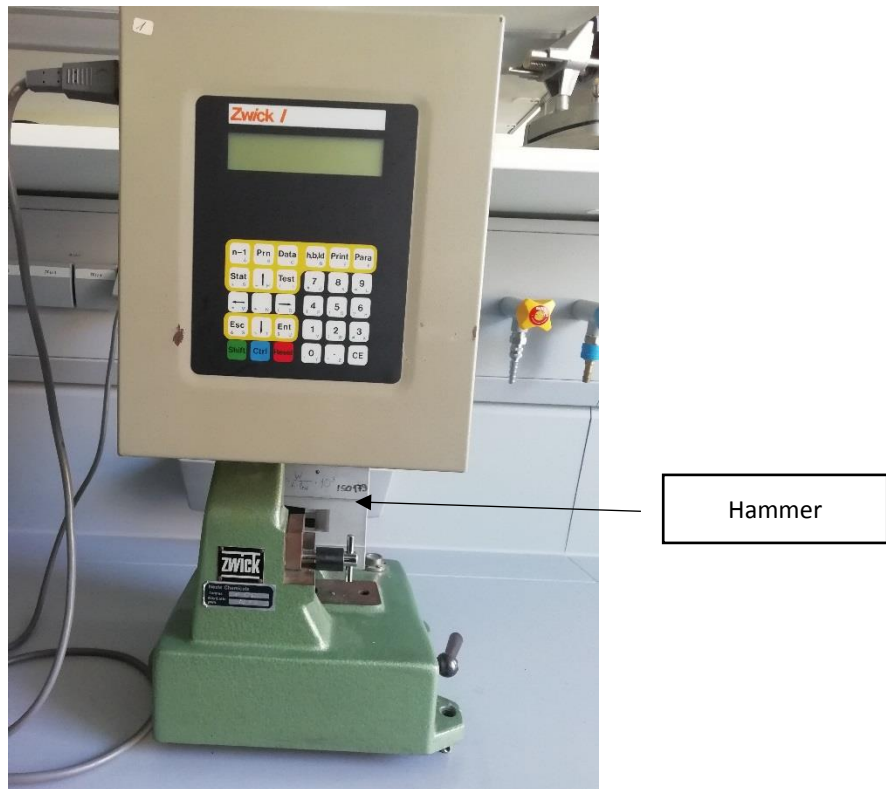


Figure 2.6 Charpy impact strength machine (Author's photo)



Figure 2.7 Notched sample (Author's photo)

The formula for the calculation:

a_{cN} = Charpy impact strength in KJ/m^2

$$a_{cN} = \frac{W}{hxb_N} \times 10^3$$

W= corrected energy in joules, absorbed by breaking the test specimen

h= thickness, in millimetres of the test specimen= 4 mm= 0.004 m

b_N = remaining width, in millimetres at the notch base of the test specimen= 8 mm=0.008 m

2.5 Colourimetry

The colourimeter (Konica Minolta) (figure 2.8) used to estimate the colour. The buckles were placed on the lens of the colourimeter and measured. The values of L*, a* and b* were collected for each fastener, and ΔE^*_{ab} was calculated.

L* defines lightness; a* denotes the red/green value and b* the yellow/blue value.

$\Delta L = L_0 - L_n$; where L_0 at 0 hours and $n = 100$ h, 200 h, 300 h, 400 h respectively.

The values for Δa and Δb was calculated similarly as ΔL .

The following table gives a rating of the changes in the colour using ΔE^*_{ab} ,

ΔE^*_{ab} is expressed as, $\sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$

The colour change cannot be detected visually in all conditions. Therefore, specific changes in colour can be measured using the following Table 3. The rating of ΔE^*_{ab} helps to identify the colour change both visual and not visual.

Table 4: Rating of colour change (Hugh, 1989)

ΔE^*_{ab}	Rating
0,00-1,70	5(no change)
1,71-3,40	4 (weak)
3,41-6,80	3(little)
6,81-13,60	2(certain)
13,61-∞	1(big)



Figure 2.8 Colorimeter (Author's photo)

2.6 Calorimetry

ISO 11357-6,2008 is being followed, which specifies methods for the determination of oxidation induction time (isothermal OIT) and oxidation induction temperature of polymeric materials employing differential scanning calorimetry (DSC). Perkin- Elmer DSC 7 model was used to perform the experiment. This technique applies to stabilised or compounded form of polyolefins.

Steps involved in conducting a DSC experiment are as follows:

- The specimen in the range of 2.00 mg-2.50 mg were wrapped into aluminium foil. An empty foil was used as a reference sample.
- The samples were heated in nitrogen to prevent from thermal oxidation, from 50°C and kept at 220°C.
- The atmosphere was changed to oxygen for 20 mins.
- After changing to oxygen, the time to exothermic peak was measured.
- Pyris Software was used to analyse all the data.

The melting and crystallization temperature were conducted following ISO 11357-3:2011 standard. The melting point of the samples were obtained in the absence of oxygen and was kept in 220°C for 10 mins.

3 Results & Discussions

The mean of the collected data was calculated. The test data are recorded in the appendix of the paper.

3.1 Tensile testing

The samples at 0 h had a different type of deformity compared to the samples which were under the influence of temperature (Figure 3.1, 3.2, 3.3, 3.4, 3.5). It was noted that aged samples after the test curled up whereas the samples at 0 h stretched until broke.

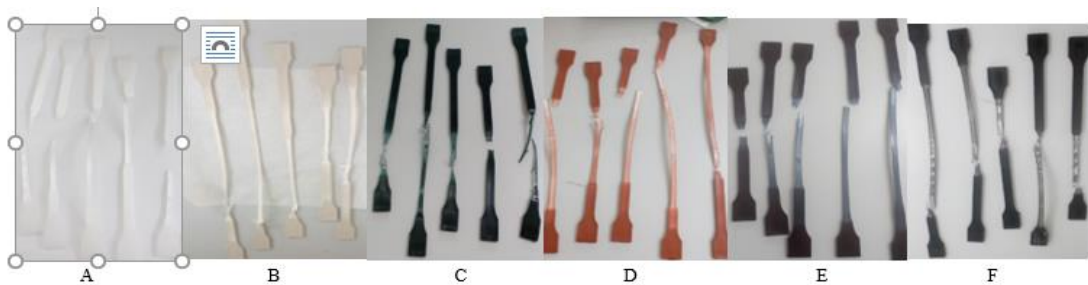


Figure 3.1 Tensile tested samples at 0 h (Author's photo)

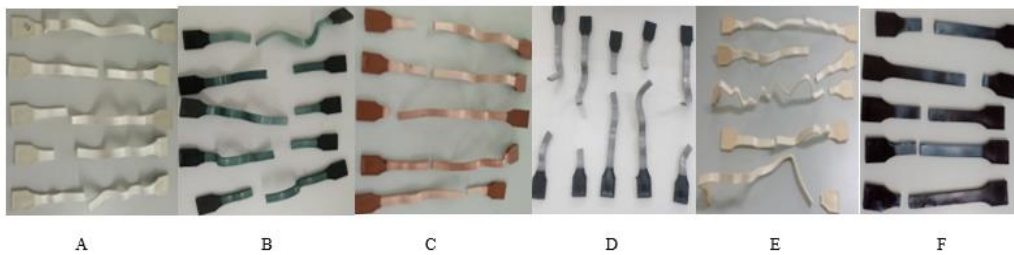


Figure 3.2 Tensile tested samples at 100 h (Author's photo)

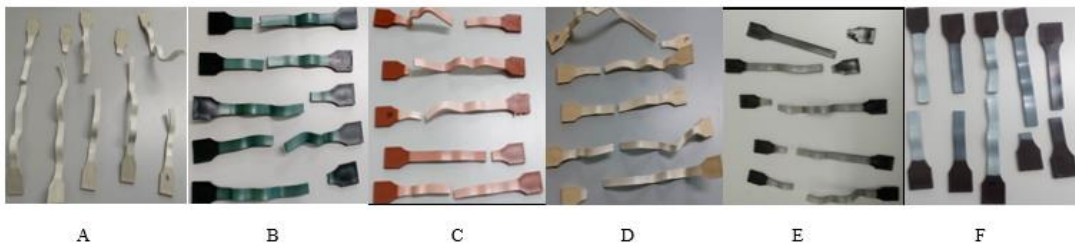


Figure 3.3 Tensile tested samples at 200 h (Author's photo)



Figure 3.4 Tensile tested samples at 300 h (Author's photo)



Figure 3.5 Tensile tested samples at 400 h (Author's photo)

The average stress at maximum load and the standard deviation of the average tensile stress was calculated using the bluehill software, and then all the data was compared. The black colour shows the maximum stress at maximum load for all the ageing hours. But the Cambrian green coloured samples decreased with the increase in the ageing hours. The stress at maximum load for magnolia, linen and damson coloured samples remained in a similar range from 22-23MPa. Comparison to pure PP, the black coloured specimen shows higher stress value and the other colours are not as good as the pure PP (Figure 3.6). There is no trend which can be followed for all the colour.

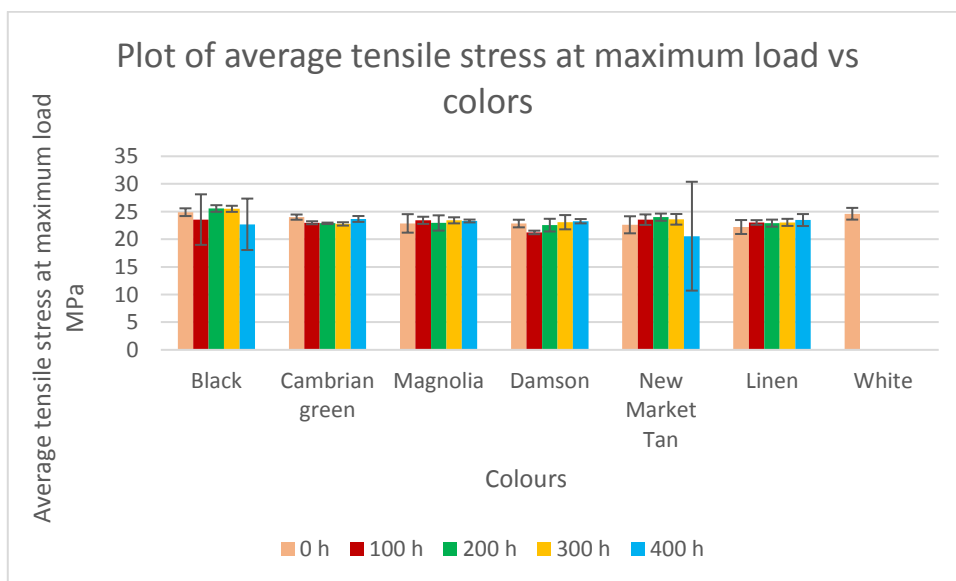


Figure 3. 6 Plot of average tensile stress at maximum load vs colours

The colourants influenced the tensile strain compared to the pure PP sample. The elongation has increased for all the coloured samples compared to the matrix PP. The strain at break for black has increased slightly (47 %-113 %) with the increasing ageing time. The elongation of magnolia coloured samples has risen by nearly 200 % times more than pure PP. Damson has the least average strain for all time intervals (exception 0 hours). At 100 h and 400 h, it is even lower than the natural PP. The standard deviation changed according to ageing time, either increased or decreased. Newmarket tan has strain value in a range of 140-120 % (exception: 175.56 % at 100 hours), and the standard deviation is in a variety of 30-39 %. None of the colours has a trend of increasing or decreasing elongation regarding the ageing time.

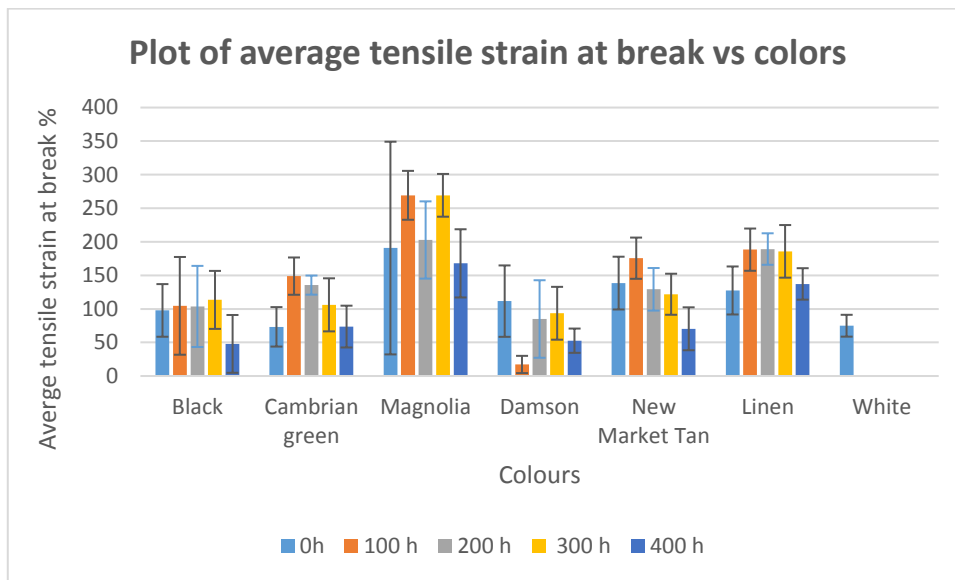


Figure 3.7 Plot of average tensile strain (in %) at break vs colours

3.2 Charpy Impact test

The impact strength of coloured samples was higher compared to pure PP. In many cases, the impact strength increased initially with thermal ageing time and then decreased again for the longest time, 400 h. The black coloured specimen has a gradual increase in the impact strength from 0 h to 400 h. The highest value is 14,90 KJ/m² at 400 h and least 10,18 KJ/m². Cambrian green samples show inevitable fluctuations in the impact strength values. At 100 h green coloured specimen has the highest value 42,96 KJ/m², and the lowest is 15,68 KJ/m². The magnolia samples have the highest amount of impact strength at all the ageing time intervals, except at 0 h. The highest value is 46,67 KJ/m². The black coloured pieces have the minimum impact strength at 0 h, i.e. 10,18 KJ/m² among all the colours. In the case of Damson coloured samples, there is a decrease in value from 100 h to 400 h. Black has a trend where the strength is increasing with the increasing ageing time. The impact strength is decreasing for green and magnolia after from 100 h to 400 h. The discussions above can be followed in figure 3.8.

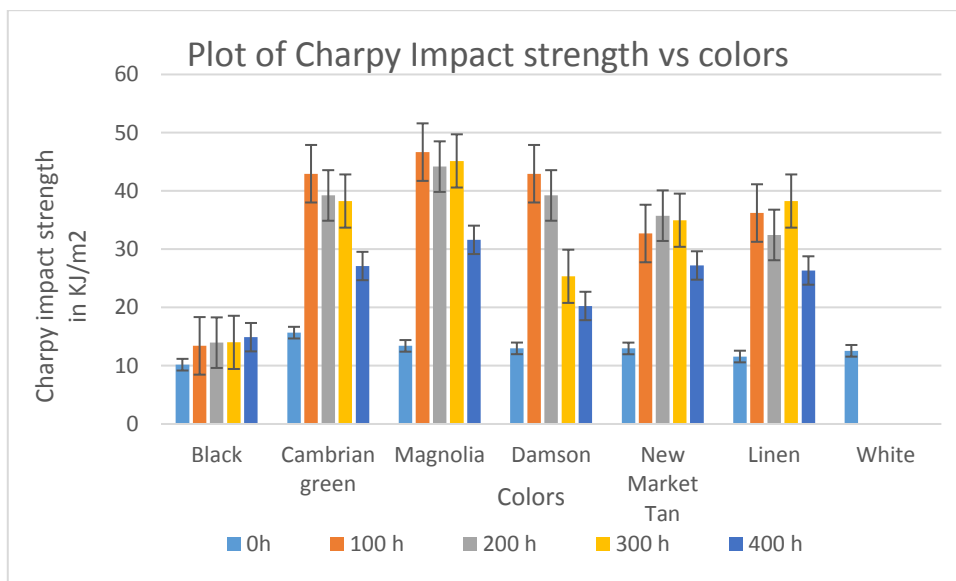


Figure 3.8 Plot of Charpy impact vs colours

3.3 Colourimetry

The red line in the graph refers to a visually detectable difference in colours (Table 3). The black and green coloured samples have very low ΔE^*_{ab} (nearly less than) which indicates that there is no colour change, but the ΔE^*_{ab} increased slightly with the increasing ageing time (Figure 3.9). The damson coloured samples also have ΔE^*_{ab} lower than two, but the values are higher compared to black and green colour. There is a small amount of effect of ageing since the colour change is not detectable to the naked eye. The maximum ΔE^*_{ab} value is 4.3 (magnolia at 400 h) which indicates little colour change mathematically. The ΔE^*_{ab} is increasing with the increase in ageing time (exception linen at 200 h). According to visual observation there is change in colour, but instrumental observation showed colour changes for magnolia and linen coloured samples.

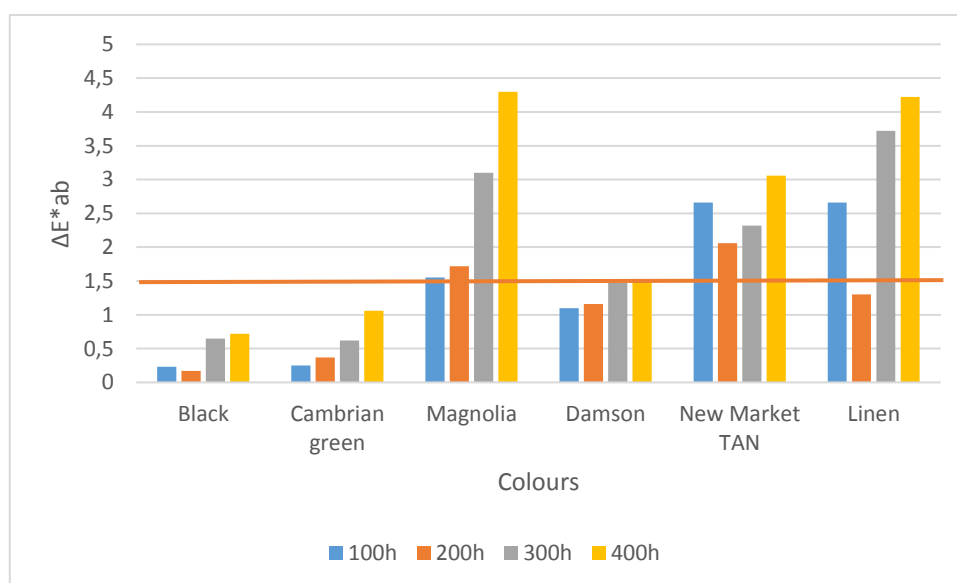


Figure 3.9 Plot of colourimetry vs colours

3.4 Calorimetry

The oxidation induction time from calorimetry is decreasing with every increasing hour compared to the pure polypropylene, which is used as a reference. The oxidation induction time is higher for the coloured samples compared to the reference (pure PP) (Figure 3.10). The specimens at 0 h show higher value and gradually decreases with the increase in ageing time. The coloured magnolia samples show the maximum OIT, i.e. 12,4 mins at 0 h among all the colours. Black and coloured magnolia samples are less affected by OIT from 0 h to 200 h but at 400 h OIT values drops quickly to 2 mins. At 200 h green, linen, damson and new market tan OIT is comparable to the reference. The OIT values for most of the colours are low at 400 h compared to reference. But the OIT of black colour at 400 h is around 4 mins, which is nearly the value of reference.

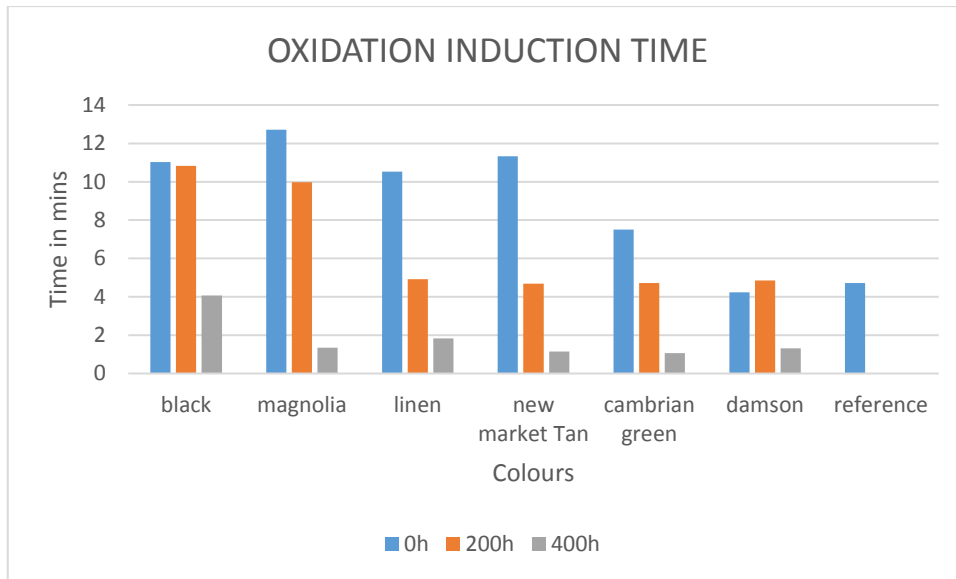


Figure 3.10 Plot of oxidation induction time vs colours

In the case of the melting point, the trend is the opposite of the OIT. The melting point is increasing with the increase in thermal ageing time. The melting point of Damson coloured samples increased by 30°C compared to the reference and all colours.

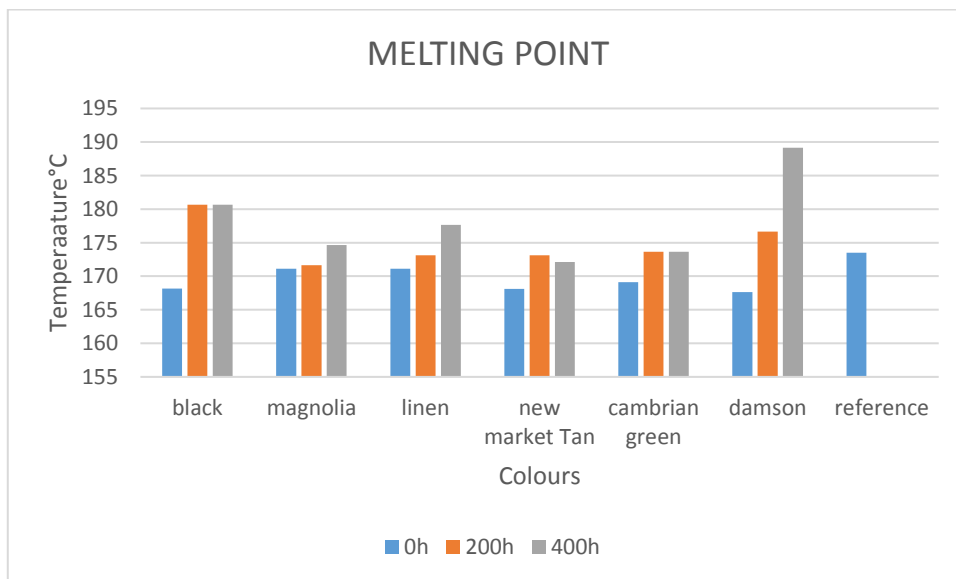


Figure 3.11 Plot of melting point vs the colours

Conclusion

During the study, the samples were successfully injection moulded with the colourants. The ageing of the samples at 150°C was not successful in the case of pure PP. After completion of 100 h, the pure PP had to be discarded since it melted and contaminated a few other samples in the sample.

The tests were conducted to receive an overview of the effect of colourants on the mechanical and chemical behaviour of polypropylene. The tensile tests are conducted to determine the stress and strain of the material. The tensile stress increased slightly for the coloured specimens compared to pure PP. The stress value increased from 24.61 MPa (pure PP) to 25 MPa (black). The tensile strain results of coloured samples were very high compared to virgin PP. Magnolia coloured samples showed exceptionally high strain rate (250 %) among all the samples. Only the damson coloured examples show meagre (17.18 % at 100 h) elongation, indicating the brittle nature of the material. The Charpy impact test determines the amount of energy absorbed at the break. The analysis also indicates the toughness of the material and measures notched sensitivity. Although PP is a sturdy and soft material, the colourants increased the impact strength of the material as most of the values are higher than the reference value.

ΔE^*_{ab} was calculated in colourimetry. It was seen that visually there was no difference in the colour for both aged and non-aged samples. The ΔE^*_{ab} for black, green and damson was lesser than two thereby stating no colour change. Magnolia and linen coloured samples showed ΔE^*_{ab} around four, which indicates little colour change numerically. Visually none of the specimens had any colour change after prolonged ageing.

The oxidation induction time obtained from the DSC experiment decreased sharply with the increase in ageing time. OIT reduced from 10 mins to 2 mins for the coloured PP. At 400 h, OIT became even lower than the reference (4 mins). The ageing influenced the antioxidants present in the colourant. The melting point increased for all the specimens compared to reference and damson had an increase by 30°C.

However, the studies have tensile, impact strength, colour change, OIT and melting point results for PP with colourants and pure PP and more reviews is required to learn about the chemistry in the colourant.

SUMMARY

In this thesis, six different colourants along with the polypropylene as the matrix polymer were used. Colourant masterbatch (10% by weight) was used to prepare injection moulded specimens, and the samples were aged along with car buckles at 150°C for 100 h, 200 h, 300 h and 400 h. One set of samples were not under the influence of thermal ageing, which was used as a reference. The samples were tested mechanically- tensile test and Charpy impact test. A colourimeter was used to measure the change in colour. Finally, thermal properties were obtained from the DSC experiment. The tensile stress and strain increased as compared to the pure PP. The Charpy impact strength also increased for the aged samples compared to the non-aged samples, enhancing the toughness of the material. The thermal ageing affected the colour of the specimens slightly. There was no colour change visually. The OIT of the coloured samples increased as compared to the pure PP thereby indicating the presence of antioxidants. Later OIT decreased for all the colours with the increase in ageing time. Ageing influenced the melting point- it increased gradually with the increase in ageing hours. The melting point increased around 30°C. The chemistry of colourants is yet to be known for more characterisation of PP which can be done further in these studies.

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APPENDICES

A: Results of mechanical testing-Tensile test

APPENDIX A 1.1 Recorded data at 150°C at 0 hours

Colour	Average tensile stress at maximum load (MPa)	Average tensile strain at maximum load (%)	Average tensile stress at break (Standard) (MPa)	Average tensile strain at break (Standard) (%)	Standard deviation average tensile strain at break (Standard) (%)	Average energy at break (Standard) (J)	Average Modulus (Automatic Young's) (MPa)	Standard deviation tensile stress at maximum load
Black	24.89	6.48	14.03	97.74	39.23	79.62	1293.31979	0.70
Cambrian green	24.00	4.88	16.81	73.28	29.39	65.08	1352.69010	0.47
Magnolia	22.86	6.27	13.09	190.66	158.46	147.96	1174.78996	1.67
Damson	22.84	5.69	15.81	111.59	53.19	94.39	1314.99600	0.69
New Market Tan	22.61	6.42	13.06	138.48	39.30	109.11	1141.27618	1.54
Linen	22.21	6.57	13.68	127.47	35.76	99.45	1099.57327	1.26
White	24.61	5.45	15.42	74.93	16.28	62.98	1311.23860	1.06

APPENDIX A 1.2 Recorded data at 150°C at 100 hours

Colour	Average tensile stress at maximum load (MPa)	Average tensile strain at maximum load (%)	Average tensile stress at break (Standard) (MPa)	Average tensile strain at break (Standard) (%)	Standard deviation average tensile strain at break (Standard) (%)	Average energy at break (Standard) (J)	Average Modulus (Automatic Young's) (MPa)	Standard deviation tensile stress at maximum load
Black	23.55	104.20	19.74	104.54	72.84	119.63	1702.87610	4.57
Cambrian green	22.98	126.23	22.83	148.83	27.78	151.19	1691.15660	0.27
Magnolia	23.42	267.93	23.39	269.24	36.44	267.99	1438.37958	0.65
Damson	21.23	3.25	20.23	17.18	12.85	15.12	1723.80341	0.32
New market Tan	23.54	147.79	23.41	175.56	30.72	183.04	1608.15475	0.95
Linen	23.03	186.77	22.99	188.28	31.48	188.92	1544.15448	0.42

APPENDIX A 1.3 Recorded data at 150°C at 200 hours

Colour	Average tensile stress at maximum load (MPa)	Average tensile strain at maximum load (%)	Average tensile stress at break (Standard) (MPa)	Average tensile strain at break (Standard) (%)	Standard deviation average tensile strain at break (Standard) (%)	Average energy at break (Standard) (J)	Average Modulus (Automatic Young's) (MPa)	Standard deviation tensile stress at maximum load
Black	25.56	85.56	25.24	103.68	60.44	117.35	1810.69245	0.60
Cambrian green	22.88	112.00	22.75	135.46	14.25	138.11	1692.32489	0.13
Magnolia	22.94	201.15	22.87	202.69	57.55	203.49	1463.23120	1.38
Damson	22.55	54.20	21.89	84.96	57.77	86.53	1690.10757	1.15
New market Tan	23.99	111.95	23.71	129.20	31.71	138.56	1647.81949	0.65
Linen	22.91	187.74	22.39	189.19	23.46	190.01	1481.02098	0.64

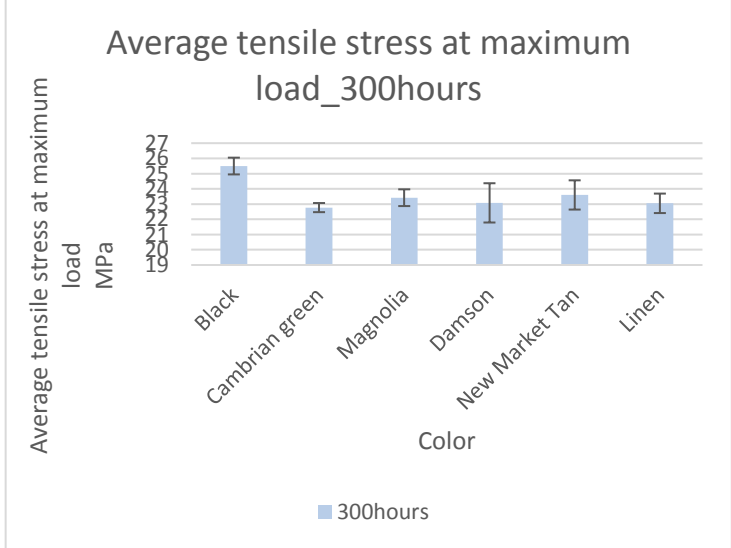
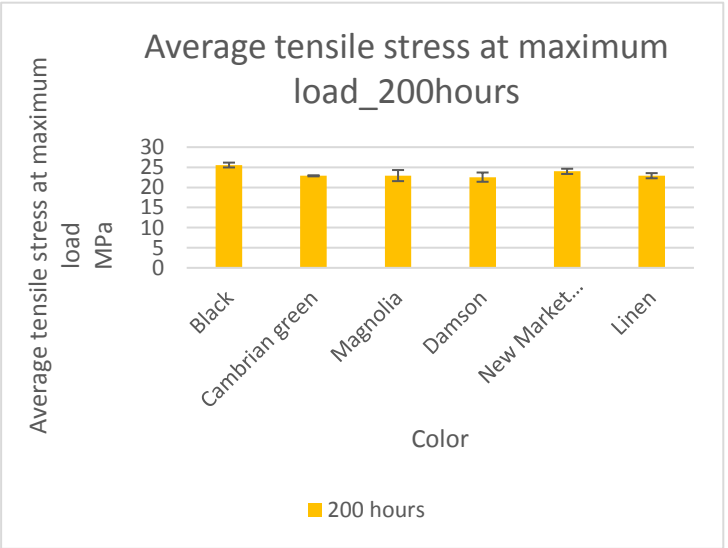
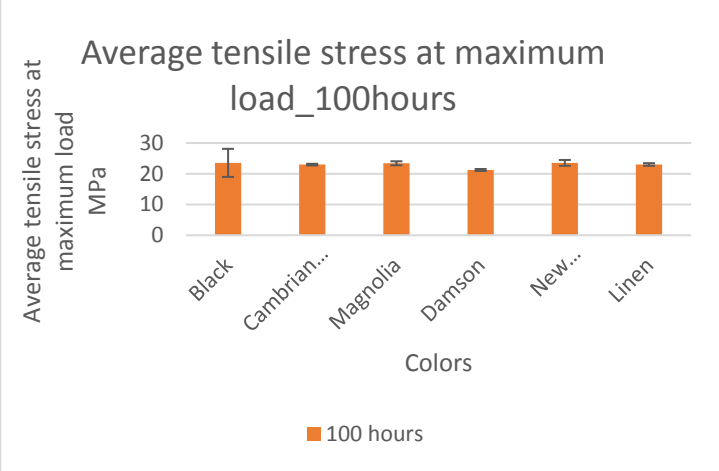
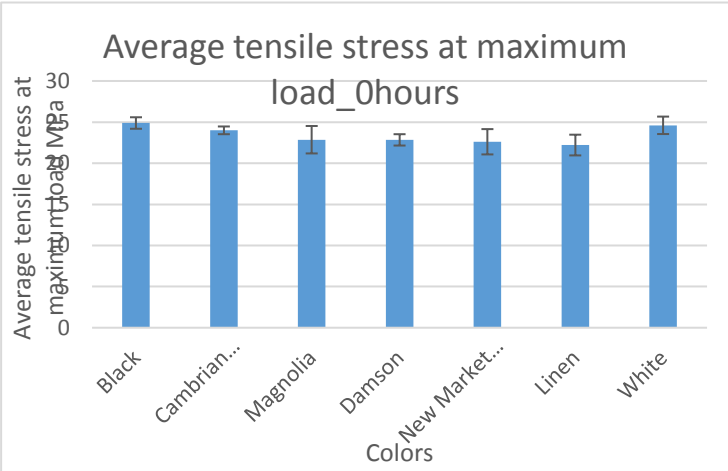
APPENDIX A 1.3 Recorded data at 150°C at 300 hours

Colour	Average tensile stress at maximum load (MPa)	Average tensile strain at maximum load (%)	Average tensile stress at break (Standard) (MPa)	Average tensile strain at break (Standard) (%)	Standard deviation average tensile strain at break (Standard) (%)	Average energy at break (Standard) (J)	Average Modulus (Automatic Young's) (MPa)	Standard deviation tensile stress at maximum load
Black	25.50	85.52	20.25	113.43	43.21	126.83	1829.14296	0.55
Cambrian green	22.77	56.53	22.10	106.06	39.51	106.97	1651.28034	0.30
Magnolia	23.42	267.93	23.39	269.24	31.85	267.99	1438.37958	0.55
Damson	23.08	54.70	22.57	93.49	39.36	96.49	1686.79178	1.29
New market Tan	23.60	32.34	23.22	121.83	30.59	127.26	1584.34791	0.96
Linen	23.05	185.21	23.03	185.74	39.22	186.19	1560.15272	0.64

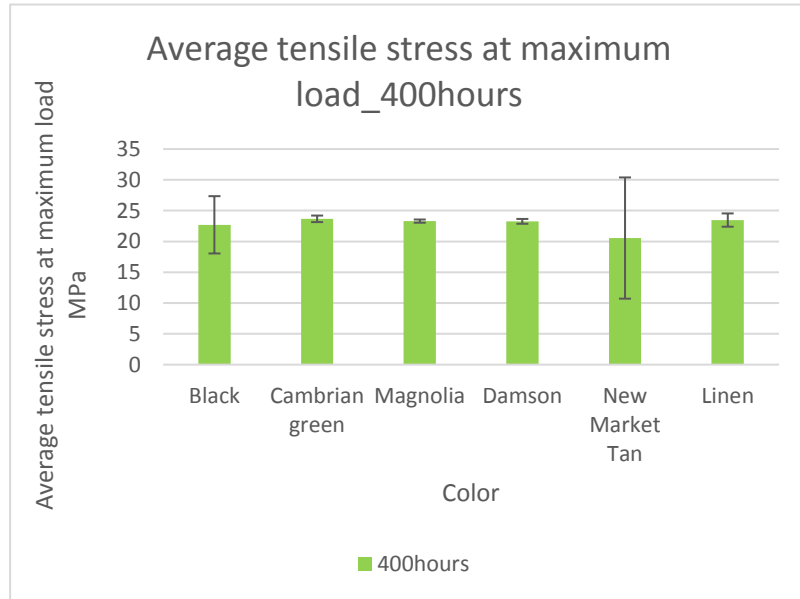
APPENDIX A 1.4 Recorded data at 150°C at 400 hours

Colours	Average tensile stress at maximum load (MPa)	Average tensile strain at maximum load (%)	Average tensile stress at break (Standard) (MPa)	Average tensile strain at break (Standard) (%)	Standard deviation average tensile strain at break (Standard) (%)	Average energy at break (Standard) (J)	Average Modulus (Automatic Young's) (MPa)	Standard deviation tensile stress at maximum load
Black	22.70	34.78	20.11	47.86	43.06	54.61	1958.67442	4.65
Cambrian green	23.67	3.10	22.31	73.67	31.15	76.02	1664.39106	0.53
Magnolia	23.30	122.33	23.14	167.85	50.80	172.29	1589.36292	0.26
Damson	23.26	3.15	21.93	52.62	18.07	52.57	1653.26929	0.39
New market Tan	20.55	3.18	19.88	70.38	31.97	75.17	1767.70408	9.84
Linen	23.47	92.75	23.31	137.22	23.44	144.31	1546.28992	1.08

APPENDIX A 1.5 Tensile stress graphs at 0, 100, 200, 300 hours

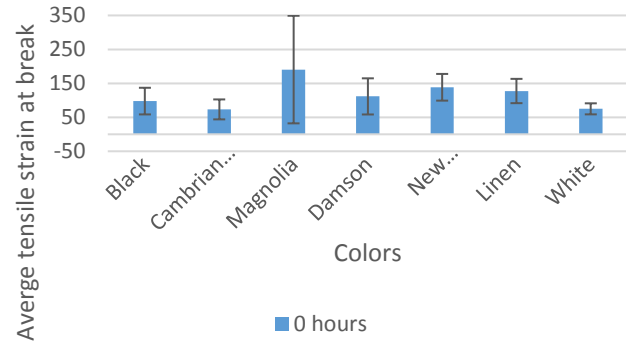


APPENDIX A 1.6 Tensile stress graphs at 400 hours

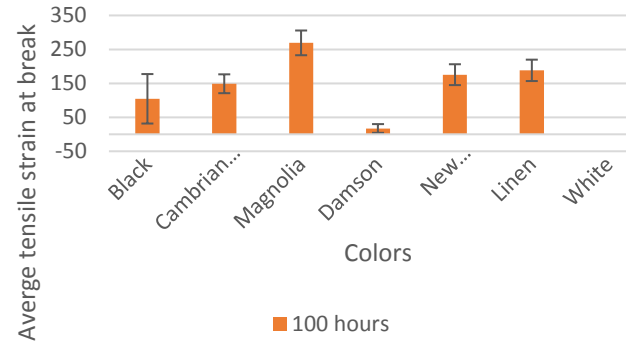


APPENDIX A 1.7 Tensile strain graphs at 0, 100, 200 and 300 hours

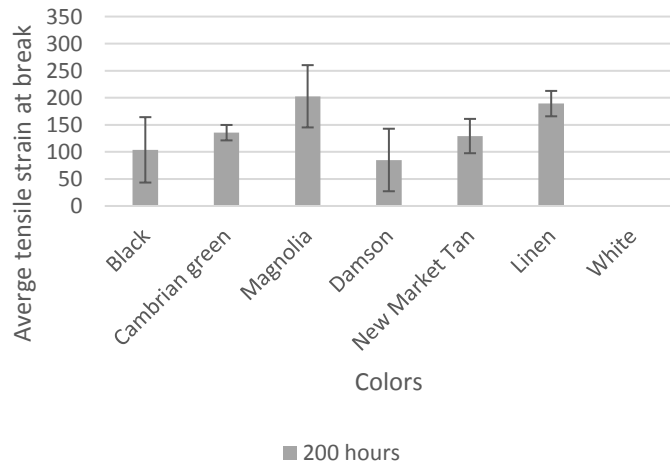
Average tensile strain at 0 hours



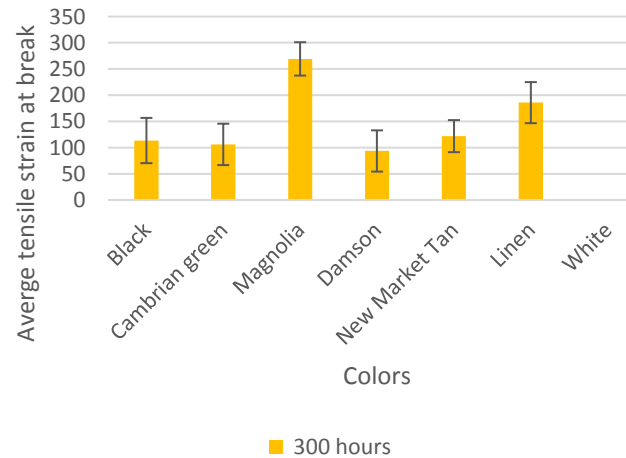
Average tensile strain at 100 hours



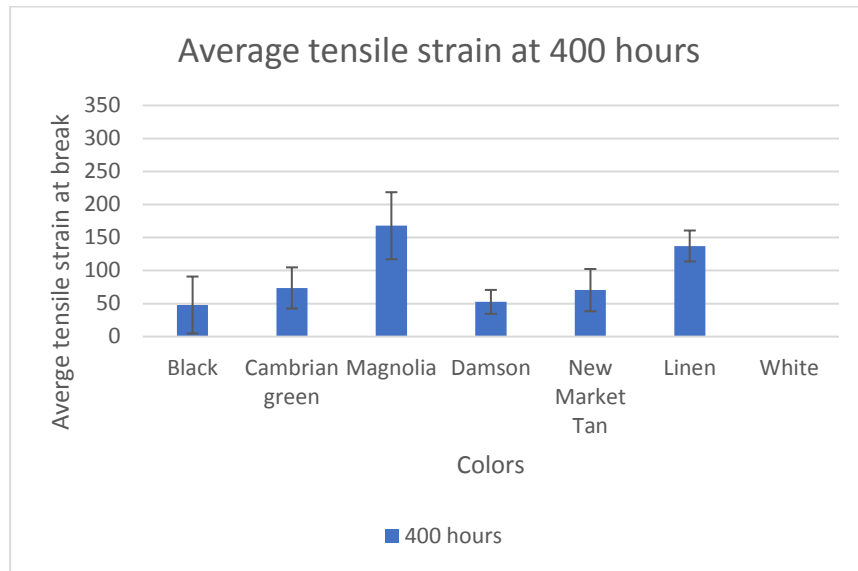
Average tensile strain at 200 hours



Average tensile strain at 300 hours



APPENDIX A 1.7 Tensile strain graphs at 400 hours



B: Results of mechanical testing-Charpy Impact Strength

APPENDIX B 1.1 Recorded data of Pure PP

Sample: White

Sample number	Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
1.	0	0,415		
2.		0,401		
3.		0,421	0,402	12,5625
4.		0,398		
5.		0,375		

APPENDIX B 1.2 Recorded data of colourants

Sample: Black

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,309, 0,344, 0,307, 0,339, 0,331	0,326	10,18
100	0,366, 0,401, 0,438, 0,524, 0,418	0,4294	13,41
200	0,441, 0,447, 0,406, 0,475, 0,465	0,4468	13,96
300	0,383, 0,392, 0,481, 0,496, 0,490	0,4484	14,01
400	0,472, 0,549, 0,450, 0,436, 0,478	0,477	14,90

Sample: Cambrian green

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,478, 0,562, 0,490, 0,490, 0,490	0,502	15,68
100	1,401, 1,414, 1,310, 1,443, 1,306	1,374	42,96
200	1,253, 1,249, 1,245, 1,277, 1,253	1,255	39,23
300	1,128, 1,164, 1,306, 1,212, 1,314	1,224	38,27
400	0,893, 0,820, 0,886, 0,900, 0,841	0,868	27,12

APPENDIX B 1.3 Recorded data of colourants

Sample: Magnolia

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,358, 0,433, 0,453, 0,401, 0,502	0,429	13,41
100	1,452, 1,510, 1,506, 1,477, 1,523	1,493	46,67
200	1,519, 1,216, 1,401, 1,473, 1,460	1,413	44,18
300	1,376, 1,523, 1,323, 1,473, 1,532	1,445	45,16
400	0,938, 1,042, 1,092, 1,030, 0,957	1,011	31,61

Sample: Damson

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,462, 0,465, 0,344, 0,392, 0,415	0,415	12,96
100	1,401, 1,414, 1,310, 1,443, 1,306	1,374	42,96
200	1,253, 1,249, 1,245, 1,277, 1,253	1,255	39,23
300	0,591, 0,912, 0,860, 0,794, 0,900	0,811	25,35
400	0,628, 0,709, 0,559, 0,685, 0,661	0,648	20,26

APPENDIX B 1.3 Recorded data of colourants

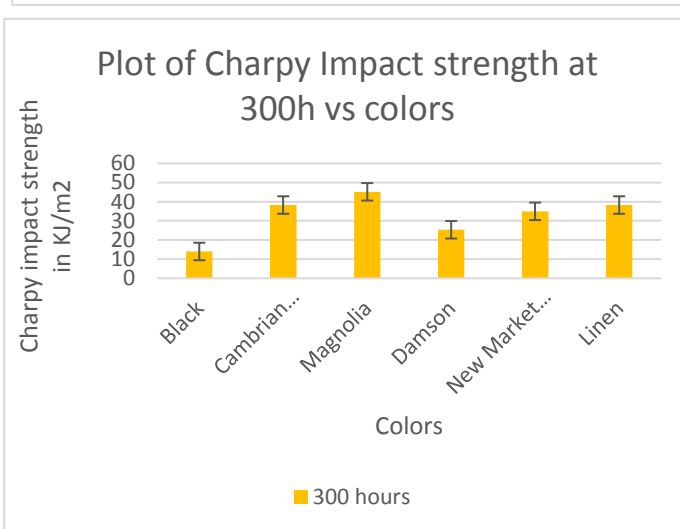
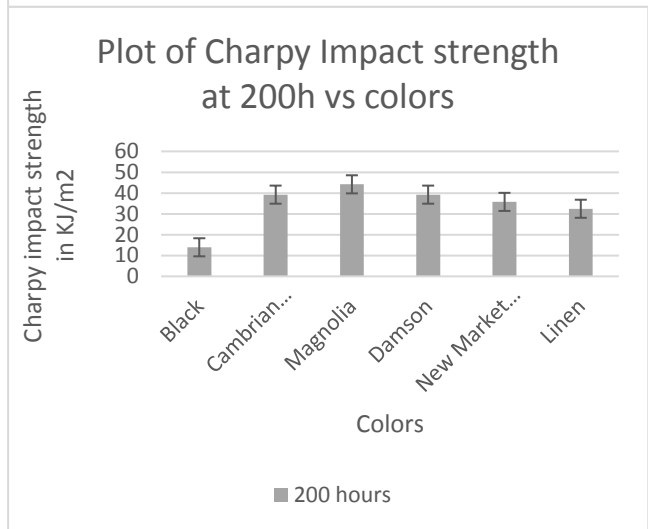
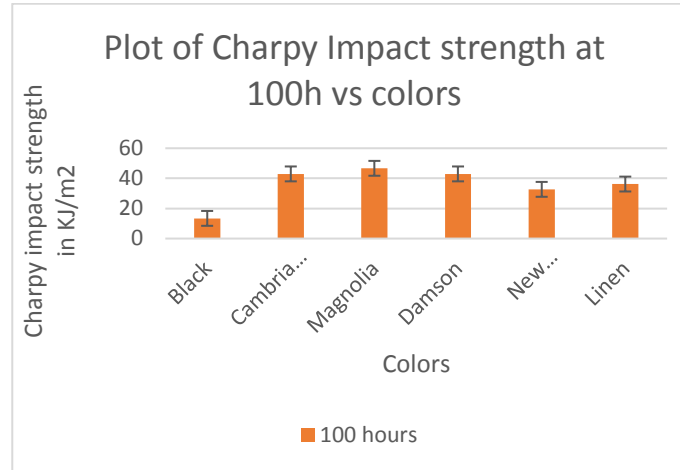
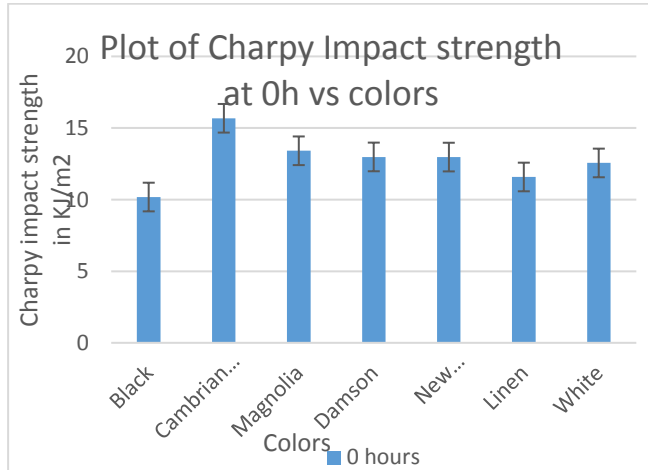
Sample: New Market Tan

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,427, 0,430, 0,415, 0,392, 0,412	0,4152	12,97
100	1,339, 0,751, 1,040, 0,706, 1,397	1,046	32,70
200	1,302, 0,820, 1,435, 0,838, 1,327	1,144	35,75
300	0,766, 1,184, 1,180, 1,112, 1,356	1,119	34,98
400	0,787, 0,871, 0,689, 0,900, 1,108	0,871	27,21

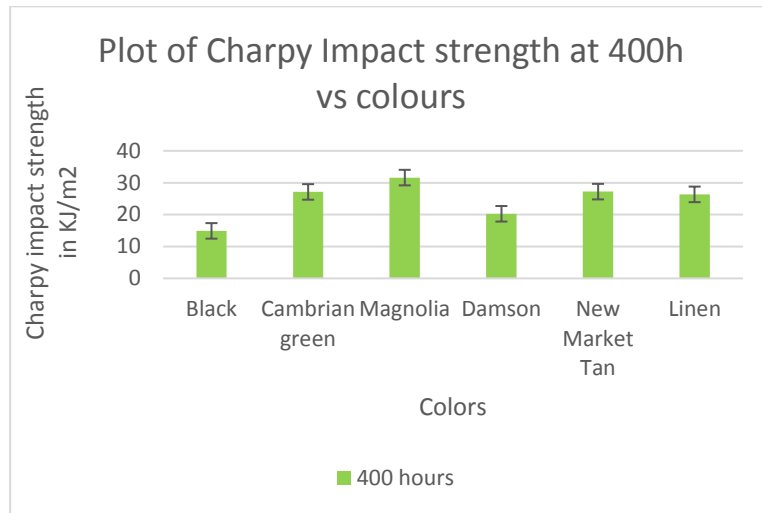
Sample: Linen

Time (hours)	W (in joules)	Average W (in joules)	acN (in kilojoules per sq. m)
0	0,381, 0,378, 0,342, 0,392, 0,361	0,3708	11,58
100w	1,286, 1,188, 1,148, 1,104, 1,069	1,159	36,21
200	1,144, 0,927, 1,018, 1,120, 0,984	1,0383	32,45
300	1,128, 1,164, 1,306, 1,212, 1,314	1,224	38,27
400	0,834, 0,900, 0,912, 0,727	0,843	26,35

APPENDIX B 1.4 Impact strength graphs at 0, 100, 200 and 300 hours



APPENDIX B 1.5 Impact strength graph at 400 hours



C: Results of colourimetry

APPENDIX C 1.1 Recorded data for L*-Lightness

Colours	0 hours	100 hours	200 hours	300 hours	400 hours
Black	25,50	25,28	25,67	24,86	24,81
Cambrian Green	28,78	28,82	28,9	28,3	27,83
Magnolia	83	81,48	82,18	80,04	78,76
Damson	28,06	27,73	32,82	40,14	28,51
New Market Tan	42,88	40,86	42,74	40,81	41,08
Linen	78,23	75,7	77,53	74,87	74,4

APPENDIX C 1.2 Recorded data for a*

Colours	0 hours	100 hours	200 hours	300 hours	400 hours
Black	-0,02	0,00	-0,02	-0,06	-0,02
Cambrian Green	-1,38	-1,25	-1,34	-1,24	-1,23
Magnolia	4,43	4,49	4,34	4,59	4,67
Damson	4,69	3,89	1,83	-0,71	3,66
New Market Tan	20,46	19,25	19,66	19,01	18,71
Linen	1,25	1,13	1,05	1,09	1,25

APPENDIX C 1.3 Recorded data for b*

Colours	0 hours	100 hours	200 hours	300 hours	400 hours
Black	-1,05	-0,98	-1,02	-0,92	-0,85
Cambrian Green	-0,05	0,16	0,3	0,31	0,4
Magnolia	21,61	21,91	22,22	22,5	22,27
Damson	-1,54	-0,86	-1,91	-0,71	-0,65
New Market Tan	20,62	19,39	29,09	19,37	18,87
Linen	9,33	10,15	10,41	10,93	11,1

APPENDIX C 1.4 Calculated data for ΔE_{100} and ΔE_{200}

Colours	L0	L100	dL	a0	a100	da	b0	b100	db	E0-100
Black	25,50	25,28	-0,22	-0,02	0,00	0,02	-1,05	-0,98	0,07	0,23
Cambrian green	28,78	28,82	0,04	-1,38	-1,25	0,13	-0,05	0,16	0,21	0,25
Magnolia	83	81,48	-1,52	4,43	4,49	0,06	21,61	21,91	0,30	1,55
Damson	28,06	27,73	-0,33	4,69	3,89	-0,80	-1,54	-0,86	0,68	1,10
New Market TAN	42,88	40,86	-2,02	20,46	19,25	-1,21	20,62	19,39	-1,23	2,66
Linen	78,23	75,7	-2,53	1,25	1,13	-0,12	9,33	10,15	0,82	2,66

Colours	L0	L100	dL	a0	a200	da	b0	b200	db	E0-200
Black	25,50	25,67	0,17	-0,02	-0,02	0,00	-1,05	-1,02	0,03	0,17
Cambrian green	28,78	28,9	0,12	-1,38	-1,34	0,04	-0,05	0,3	0,35	0,37
Magnolia	83	81,37	-1,63	4,43	4,51	0,08	21,61	22,15	0,54	1,72
Damson	28,06	27,89	-0,17	4,69	3,76	-0,93	-1,54	-0,87	0,67	1,16
New Market TAN	42,88	41,35	-1,53	20,46	19,36	-1,10	20,62	19,78	-0,84	2,06
Linen	78,23	75,4	-2,83	1,25	1,05	-0,20	9,33	10,58	1,25	3,10

APPENDIX C 1.5 Calculated data for ΔE_{300} and ΔE_{400}

Colours	L0	L300	dL	a0	a300	da	b0	b300	db	E0-300
Black	25,50	24,86	-0,64	-0,02	-0,06	-0,04	-1,05	-0,92	0,13	0,65
Cambrian green	28,78	28,3	-0,48	-1,38	-1,24	0,14	-0,05	0,31	0,36	0,62
Magnolia	83	80,04	-2,96	4,43	4,59	0,16	21,61	22,5	0,89	3,10
Damson	28,06	28,96	0,90	4,69	3,92	-0,77	-1,54	-0,67	0,87	1,47
New Market TAN	42,88	42,21	-0,67	20,46	18,94	-1,52	20,62	19	-1,62	2,32
Linen	78,23	74,87	-3,36	1,25	1,09	-0,16	9,33	10,93	1,60	3,72

Colours	L0	L400	dL	a0	a400	da	b0	b400	db	E0-400
Black	25,50	24,81	-0,69	-0,02	-0,02	0,00	-1,05	-0,85	0,20	0,72
Cambrian green	28,78	27,83	-0,95	-1,38	-1,23	0,15	-0,05	0,4	0,45	1,06
Magnolia	83	78,76	-4,24	4,43	4,67	0,24	21,61	22,27	0,66	4,30
Damson	28,06	28,78	0,72	4,69	3,83	-0,86	-1,54	-0,53	1,01	1,51
New Market TAN	42,88	41,08	-1,80	20,46	18,71	-1,75	20,62	18,87	-1,75	3,06
Linen	78,23	74,4	-3,83	1,25	1,25	0,00	9,33	11,1	1,77	4,22

D: Results of calorimetry

APPENDIX D 1.1 Recorded data for Melting point, crystallization point and oxidation induction time

Melting point and crystallization point

Reference T_m=173.52 T_c=108.28

Colour	0hours		200hours		400hours	
	T _m	T _c	T _m	T _c	T _m	T _c
Black	168,16	112,61	180,64	113,58	180,65	114,07
Magnolia	171,13	113,07	171,63	112,58	174,64	113,08
Linen	171,13	113,07	173,14	115,57	177,64	111,07
New Market Tan	168,13	116,06	173,14	116,08	172,13	117,07
Cambrian Green	169,13	124,08	173,64	125,08	173,64	125,57
Damson	167,64	130,58	176,64	130,49	189,15	130,58

Oxidation Induction Time (in mins)

Reference =4.717min

Colour	0hours	200hours	400hours
Black	11,029	10,83	4,072
Magnolia	12,715	9,973	1,339
Linen	10,525	4,922	1,825
New Market Tan	11,322	4,691	1,145
Cambrian Green	7,5	4,712	1,067
Damson	4,241	4,845	1,311